Near- and Mid-Infrared Diffuse Reflectance Spectroscopy for Measuring Soil Metal Content

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ABSTRACT

Rapid and nondestructive methods such as diffuse reflectance infrared spectroscopy provide potentially useful alternatives to time-consuming chemical methods of soil metal analysis. To assess the utility of near-infrared reflectance spectroscopy (NIRS) and diffuse mid-infrared reflectance spectroscopy (DRIFTS) for soil metal determination, 70 soil samples from the metal mining region of Tarnowskie Gory (Upper Silesia, Poland) were analyzed by both chemical and spectroscopic methods. Soils represented a wide range of pH (4.0–8.0), total carbon (5.1–73.2 g kg^{-1}), and textural classes (from sand to silty clay loam). Soils had various contents of metals (14–4500 mg kg^{-1} for Zn, 18–6530 mg kg^{-1} for Pb, and 0.17–34 mg kg^{-1} for Cd), ranging from natural background levels to high contents indicative of industrial contamination in the region. Soil samples were scanned at the wavelengths from 400 to 2498 nm (near-infrared region) and from 2500 to 25 000 nm (mid-infrared region). Calibrations were developed using the one-out validation procedure under partial least squares (PLS) regression. Mid-infrared spectroscopy markedly outperformed NIRS. Iron, Cd, Cu, Ni, and Zn were successfully predicted using DRIFTS. The coefficients of determination (R^2) between actual and predicted contents were 0.97, 0.94, 0.80, 0.99, and 0.96 for those metals, respectively. Only Pb content was predicted poorly. Calibrations using NIRS were less accurate. Root mean squared deviation (RMSD) values were from 1.27 (Pb) to 3.3 (Ni) times higher for NIRS than for DRIFTS. Results indicate that DRIFTS may be useful for accurate predictions of metals if samples originate from one region.

D ETAILED MONITORING of trace metals content in soils is needed, especially in regions under present or former influence of industrial activities due to the elevated risk of metal transfer to the food chain. Recognition of soil metals status in such areas forms a basis for appropriate land use, including indication of "risk spots" that should be excluded from agricultural food and fodder production or subject to remediation. Databases and maps are produced by spatial analysis of metals content in geo-referenced samples. Such regional-scale monitoring programs usually require analysis of great numbers of soil samples with limited resources. Conventional methods of metals determination in soil are based on wet digestion of soil samples in hot concentrated acids followed by inductively coupled plasma or atomic absorption spectrometric (AAS) measurements of metals in extracts (Hossner, 1996), and are time-consuming and expensive.

Two spectral ranges are generally used for analytical purposes in diffuse reflectance applications: near-infrared (NIR, 400–2500 nm) and mid-infrared (MIDIR, 2500–25 000 nm). Both NIRS and DRIFTS are nondestructive rapid analyses that under common application require no sample treatment except for grinding and mixing. Application of infrared techniques for metals determination would substantially simplify analyses and decrease their cost.

There are data suggesting that infrared spectroscopy (both NIRS and DRIFTS) combined with statistical transformation of the data could feasibly be used for accurate prediction of various soil or manure parameters such as total C, total N, or ammonia N (Reeves, 2001; Reeves et al., 2001). The technique is based on calibration equations produced for prediction of soil parameters using chemical data from conventional analysis and spectral data from scans in NIR or MIDIR regions. Basically, regression analysis is used to extract the spectral information most related to the analyte in question (e.g., metal content). This results in what is known as the calibration equation, which can then be used with new spectra to determine the analyte values of samples without the need for laboratory determinations.

Near-infrared reflectance spectroscopy has been developed as a routine technique in quantitative and qualitative determination of various parameters in the food, agriculture, textile, petrochemical, and pharmaceutical industries. Near-infrared spectroscopy gives information on the structure of organic matter since it is based on absorbance bands for bonds between C or O and H, and N and H found in proteins, cellulose, carboxyl, amide, or amino acids, etc. (Malley, 1998). More or less quantitative use of NIRS for determination of physical, chemical, and biological soil properties such as moisture; total C, N, and P contents; mineral N; quality of organic matter; and biological parameters of soil such as respiration and microbial biomass has been demonstrated (Palmborg and Nordgren, 1993; Fritze et al., 1994; Chodak et al., 2002; Confalonieri et al., 2001; Slaughter et al., 2001; Smith et al., 2001; McCarty et al., 2002). Near-infrared spectroscopy has been also used to predict trace metal content in sediments or soils (Malley and Williams, 1997; Kemper and Sommer, 2002). Malley and Williams (1997) obtained accurate predictions of metals such as Fe, Mn, Zn, Cu, Pb, and Ni in freshwater sediments despite low contents of some of them (Zn < 60 mg kg^{-1}, Cu < 50 mg kg^{-1}, Pb < 45 mg kg^{-1}, and Ni < 30 mg kg^{-1}). Normalizing parameters that the authors used were standard deviation of predicted set/standard error of prediction (RPD) and range/standard error of prediction

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(RER), which were indicative of effective calibrations for those metals. The worst calibration was produced for Cd, which was artificially added to lake water several years before the sample collection. Different behavior of the latter metal was attributed to its shorter time in the lake and its different association with inorganic and organic components as compared with other metals (Malley and Williams, 1997). The sediment samples varied widely in organic matter content (2–425 g C kg^{-1}). Kemper and Sommer (2002) used NIRS to produce calibrations for predictions of trace elements in soils contaminated by high metal sludge after a mining accident in Aznalcollar, Spain. They obtained very accurate predictions of some trace elements (Pb, Hg) while results for Zn, Cd, and Cu were not satisfactory. In the case of forage crop analysis by NIR, the content of inorganic elements is low relative to the organic matrix so their direct influence on NIR spectra may not be significant. Thus, successful calibrations for inorganic components in forage crops could be based on the effects of the inorganic material with the organic constituents, or even due to correlations between the two, and thus are often called surrogate calibrations (Shenk et al., 1992). The effect of minerals on soil spectra in the NIR region is perhaps more important since content of mineral fraction in dry matter of mineral soils is more than 90%.

Mid-infrared spectroscopy detects both absorbance by organic bonds and mineral components. The technique has been extensively used for qualitative analysis by spectral interpretation (Colthup et al., 1990) and more recently for quantitative analysis of a wide range of agricultural materials including grain, forages, manures, and soils (Janik and Skjemstad, 1995; Reeves, 1996, 2001; Reeves et al., 1999, 2001). The reason for the recent use of DRIFTS for quantitative analysis of such products was a belief that dilution of samples with KBr was necessary, which has been shown not to be true (Reeves, 2003). Mid-infrared spectroscopy has been used for quantitative analyses of soil chemical parameters less frequently than NIRS. Recent studies have shown its utility for determination of nitrates (Ehsani et al., 2001) and total carbon and nitrogen contents (Reeves et al., 2001; McCarty et al., 2002).

There is little data available to compare the utility of NIRS and DRIFTS calibration models developed for soils with diverse properties. Often NIRS calibrations have been developed using sets of soil from the same origin or similar chemical and physical characteristics. Good predictions with such sets of samples can be due to a wide range of the predicted parameter with much less variability of other soil parameters. The crucial question for utility of chemometric methods is whether they provide accurate predictions for sets of diverse soils. In a study conducted by McCarty et al. (2002), MIDIR calibrations performed significantly better than NIR calibrations for the determination of total C content. To our knowledge, this study is the first attempt to compare NIRS and DRIFTS feasibility in measuring metal contents in diverse soils.

The objective of this study was to compare the ability

of NIRS and DRIFTS to predict trace metal contents in diverse mineral soils and assess their potential utility for estimating metal contamination in soils at regional levels.

MATERIALS AND METHODS

Sample Collection

Seventy geo-referenced samples were collected from arable lands of the Tarnowskie Gory area in Poland. Approximately 1-kg soil samples were removed from the 0- to 20-cm layer using a soil core sampler. Sampling sites were located in 10 districts of Tarnowskie Gory: Strzybnica, Rybna, Tarnowice Str, Repty, Sowice, Bobrowniki, Miasteczko Slaskie, Zyglin, and Tarnowskie Gory town (Fig. 1). Soils were collected throughout the region to ensure a wide range of soil properties such as organic matter or clay content as well as metals contents. Location of sampling points within districts was dependent on distribution of arable parcels.

Tarnowskie Gory is a metal mining area located in the central part of the Silesia (Slaskie) administrative region (voivodship), which is the most industrialized region of Poland (for depiction of this region see Fig. 1). Tarnowskie Gory area is one of the most contaminated parts of that region. The presence of Zn and Pb ores has lead to development of mining and smelting industries in the region around Tarnowskie Gory. Ore mining activities in the area were started in the 12th century, and soils in the region were subjected to strong industrial emissions especially in second half of the 20th century. The biggest mine in the area was located near the town of Tarnowskie Gory in the southwest direction, and a Zn ore smelter is located in Miasteczko Slaskie. Prevailing winds in the region are from the northeast, and soils within the study area were undoubtedly under the influence of smelter emissions. Tarnowskie Gory town was a center of various types of industrial production. However, contamination in the Tarnowskie Gory area is of a complex character since soils of the area were partly developed from shallow and metal-rich trias limestones and due to the occurrence of ore outcrops mixed with topsoil.

Chemical Analyses

Soil samples were air-dried, crushed, sieved through a 1-mm mesh, and homogenized. The <1-mm fraction amounted to 98 to 99% of the total soil weight. Subsamples of these soils were then ground using a roller mill for analyses of C, trace metals, and spectroscopy. Total contents of Zn, Pb, Cd, Cu, Ni, and Fe were determined. Total contents of Zn, Pb, Cd, Cu, Ni, and Fe were analyzed using the aqua regia digestion procedure (2 h hot digestion in 1:3 v/v mixture of concentrated nitric and hydrochloric acids, followed by refluxing in 3 M hydrochloric acid) (McGrath and Cunliffe, 1985). Filtrates were analyzed by atomic absorption spectroscopy. Quality control included duplication of every 10th sample and analysis of soil reference materials (SRM) every 20 samples: NIST 2709 (baseline metals contents) and NIST 2710 (highly elevated metal contents) (National Institute of Standards and Technology, Gaithersburg, MD). The measured contents of metals in NIST reference materials were within the required range. Precision of analysis was defined as percentage relative standard deviation (RSD = SD/mean of SRM replicates). The precision was 4.0 and 1.4% (Fe), 7.6 and 1.9% (Cd), 1.9 and 2.7% (Cu), 4.9 and 1.3% (Pb), 2.4 and 2.7% (Ni), and 2.8 and 1.5% (Zn) for NIST 2709 and NIST 2711, respectively.

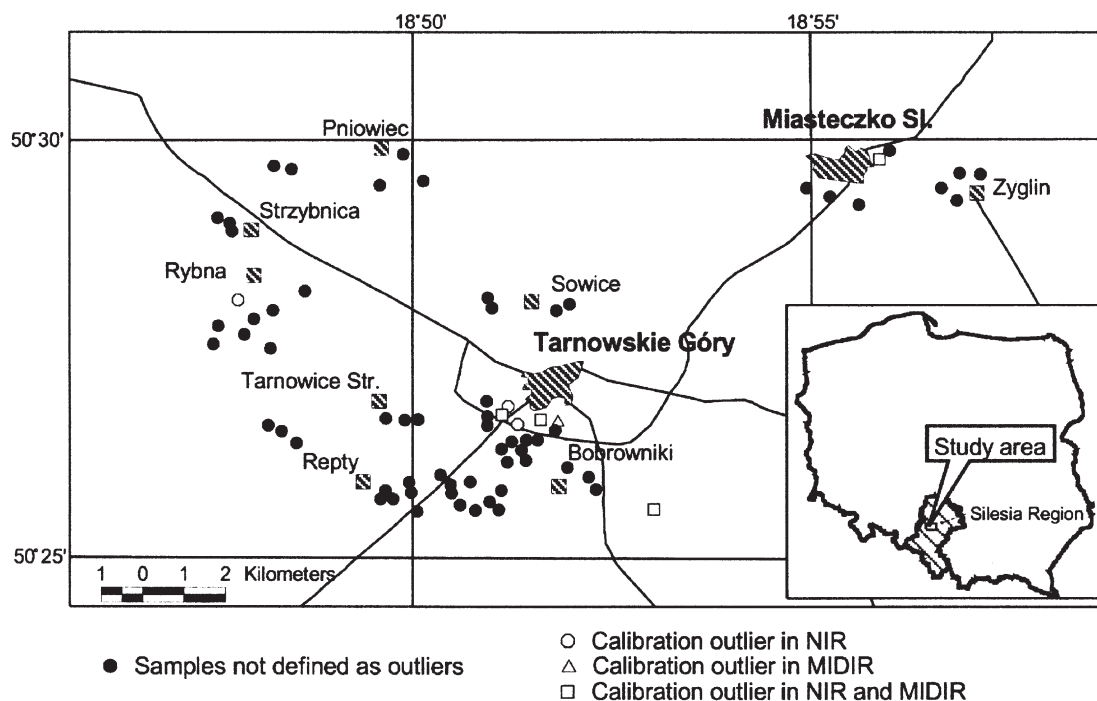Soil pH was measured in a water slurry with 1:2 v/v soil to

Fig. 1. Location of 70 sampling sites within Tarnowskie Gory region, Poland. Samples marked as empty dots, triangles, and squares are outliers in near-infrared (NIR), mid-infrared (MIDIR), or both NIR and MIDIR calibrations, respectively, for at least two metals.

solution ratio. Total C content was measured using a carbon–nitrogen–sulfur (CNS) combustion analyzer (LECO, St. Joseph, MI). Soil particle size distribution was performed by the hydrometer method (Gee and Bauder, 1986).

Spectral Measurements

Near-infrared spectra were obtained using a NIRSystems Model 6500 scanning monochromator (Foss-NIRSystems, Silver Spring, MD). Samples (5 g) were scanned from 400 to 2498 nm using a rotating cup. Data were collected every 2 nm at a resolution of 10 nm. Samples (0.5 g) were scanned in the mid-infrared region from 4000 to 400 cm^{-1} (2500 to 25 000 nm) at 4 cm^{-1} resolution with 64 co-added scans per spectra, on a DigiLab FTS-60 Fourier transform spectrometer (Bio-Rad, Richmond, CA) equipped with a custom-made sample transport that allowed a 50- $\times$ 2-mm sample to be scanned (Reeves, 1996).

Statistical Analyses and Calibrations

Descriptive statistics were calculated using SAS data analysis software (SAS Institute, 1988). All regression of NIRS and DRIFTS data was performed by partial least squares (PLS) regression using Grams/386 PLSPlus software Version 2.1G (Galactic Industries, 1992). The PLS analysis is a factor-based calibration similar to principle component regression (PCR) but produces a set of factors (model) correlated to a particular property of interest. The PLS produces factors that may or may not be directly related to spectral features associated with the specific physical or chemical properties for samples. Linear combinations of these weighted factors form the model for prediction of the property of interest. Efforts using a variety of data subsets, spectral data point averaging, derivatives (1st and 2nd), and other data transformations (mean centering, variance scaling, multiplicative scatter correction, and baseline correction) were performed to determine the best data transformation for each assay (Geladi et al., 1985).

Multiplicative scatter correction adjusts for influence of

particle-size differences, which cause differing degrees of scatter among the sample set. The coarser the sample, the deeper the radiation penetrates, which causes a baseline shift up and down. In all cases, the number of PLS factors used in the calibration was determined by the prediction residual error sum of squares (PRESS) F statistic from the one-out cross validation procedure. The best model was selected as follows: (i) for each math treatment the number of factors was selected by an F test (i.e., to determine if adding an additional factor significantly reduced the error, with a maximum of 15 factors ever being used); (ii) then the model with the lowest root mean squared deviation (RMSD) was chosen out of various math treatments; and (iii) once the optimal math treatment and number of PLS factors was determined, a final calibration was developed (Martens and Naes, 2001).

The cross-validation procedure involves removal of each sample from a set and development of a calibration equation from that set with prediction of values for the removed sample. This process is repeated for each member of the set resulting in the generation of a prediction set where each member has been treated as being independent of a calibration set. Cross-validation analysis provides information on the robustness of calibration. Calibrations were produced for entire data sets and after removal of calibration outliers. Pearson's correlation coefficients, based on ordinary least squares regression (OLS), were calculated to evaluate the significance of relationships between soil variables (Table 1).

RESULTS AND DISCUSSION

Chemical Properties

Soils collected throughout the Tarnowskie Gory area represented a wide range of major properties such as pH, organic matter, and clay content (Fig. 2). Soils were acidic to alkaline (pH 4.0–8.0). Soils had generally moderate contents of C, although high organic matter soils were also present (developed as an effect of shallow

Table 1. Correlation matrix for relationships between soil properties and metals contents.

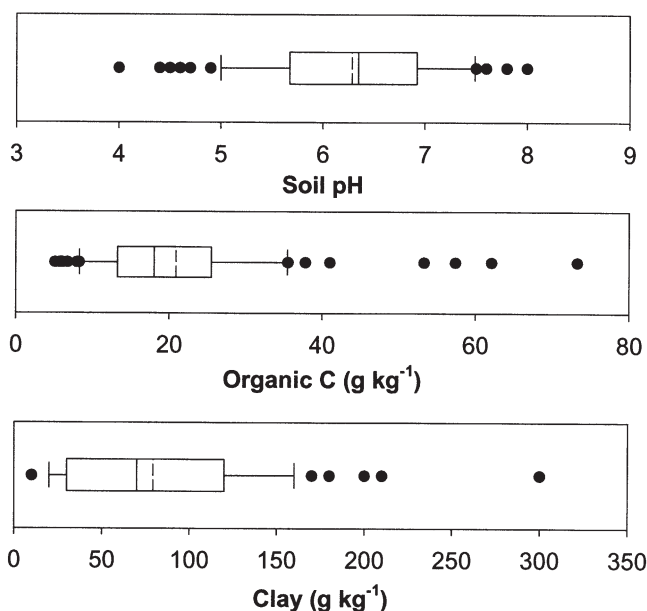|	C	pH	Clay	Fe	Cd	Cu	Pb	Ni
C								
pH	0.29*							
Clay	0.31*	0.38**						
Fe	0.43**	0.33*	0.90***					
Cd	0.60***	0.51***	0.77***	0.79***				
Cu	0.75***	0.29*	0.41**	0.57***	0.56***			
Pb	0.52***	0.24	0.69***	0.83***	0.63***	0.59***		
Ni	0.58***	0.46***	0.90***	0.95***	0.84***	0.63***	0.77***	
Zn	0.49***	0.43**	0.82***	0.88***	0.90***	0.52***	0.75***	0.85***

* Significant at the 0.05 probability level.
** Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.

ground water). Soils had various textures from sand to silty clay loam, but most soils were sandy loams or silty loams. The majority of soils in the sampling area developed from sandy or light loamy materials of glacial origin. Sandy and loamy soils occupy about 50 and 25% of arable soils of Upper Silesia, respectively (Dudka et al., 1995). Approximately 10% of the soils in the Tarnowskie Gory area developed from limestone formations (Witek et al., 1992).

Total Zn, Pb, and Cd contents in soils collected from the Tarnowskie Gory vicinity range from levels recognized as background content to highly contaminated (Fig. 3). Mean contents of these three metals in soil samples collected in a national survey program (Terelak et al., 1997) were 32.4, 13.6, and 0.21 mg kg^{-1} for Zn, Pb, and Cd, respectively, which are markedly lower than mean and even median contents in our study.
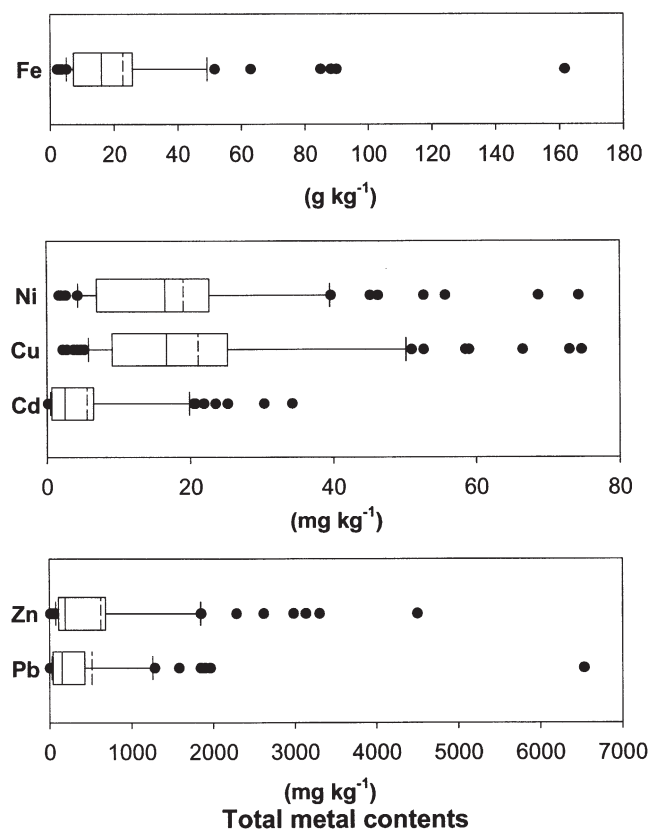
The Silesia region is an industrial area known for centuries as a site of mining and smelting of Zn and Pb ores. Industrial activities, especially intensive in the 1960s and 1970s, resulted in enrichment of Silesian soils with Zn, Pb, and Cd due to emission of smelter dusts.

A decreasing content of metals with depth in the soil profile (Witek et al., 1992) suggests a major role of industrial activities in soil contamination. Undoubtedly, metals in these soils also partly originate from pedogenic sources—parent rock material rich in metals and ore outcrops that were mixed with topsoil during years of soil cultivation (Witek et al., 1992). Significant areas of soils with elevated contents of metals in Silesia are used for agricultural production and hobby gardening resulting in notable levels of human exposure to heavy metals (Gzyl, 1990). Total Zn, Pb, and Cd contents are strongly intercorrelated in these soils (Table 1) as a result of their common pedogenic source and the likely consistent metal ratios in dusts emitted by smelters (Niec, 1997). Soils with the highest Zn content also had high contents of Pb and Cd and were located in Tarnowskie Gory and Bobrowniki (Fig. 1). High contamination of soils in the proximity of Tarnowskie Gory is mostly related to mining operations and occurrence of shallow ore outcrops.

A substantial fraction of metals in Bobrowniki soils is of natural origin. These soils were developed from metal-rich limestone formations. Soil pH for these samples ranged from 7.3 to 7.5. Metals in these soils are weakly available being precipitated as carbonates. Soils of Repty were also substantially contaminated. The soil cover of the district is diverse but mainly includes soils developed from glacial loamy materials or trias lime-

Fig. 2. Summary statistics for selected properties of soils collected in Tarnowskie Gory region. Error bars are presented with median (solid line), mean (dash line), 10th and 90th percentiles (whiskers), and all samples with property values outside 10th and 90th percentiles (dots).

Fig. 3. Summary statistics for total metal contents in soils collected in Tarnowskie Gory region. Error bars are presented with median (solid line), mean (dash line), 10th and 90th percentiles (whiskers), and all samples with metal content outside 10th and 90th percentiles (dots).

stone formations. The metals in soils of Miasteczko Slaskie mainly originate from slag emissions. The contents of Zn and Pb are high; however, metals are strongly adsorbed in soils with high clay or organic matter. Neutral and alkaline pH of soils is probably an effect of emissions of smelter dusts since no limestone formations were present in parent rock material. Surprisingly, metal contents in Zyglin are much lower, which might be related to weak sorption properties of these light, acidic soils. Zinc, Pb, and Cd contents were moderate in Rybna, Strzybnica, Sowice, and Tarnowice Str. Zinc content in these soils generally ranged between 100 and 300 mg kg^{-1}. Soils in these districts were diverse, being mainly developed from sandy or loamy materials, although calcic cambisol (Tarnowice Str.) and high organic soils (Rybna) were also present. The least contaminated soils were located in Pniowiec where metal contents were found at natural background levels.

Nickel and Cu contents in Silesian soils are not as high as Zn, Pb, and Cd according to pollution criteria since no significant sources of contamination were located in the region (Terelak et al., 1997; Kabata-Pendias and Pendias, 2001). The presence of Ni and Cu in soils within the area of interest has mainly a natural character and probably originated from pedogenic sources. This

supposition is supported by the fact that the mean contents of these metals in our study were only slightly higher than mean contents for the Silesian soils, which are 13.3 and 11.2 mg kg^{-1} for Ni and Cu, respectively (Terelak et al., 1997).

All metals contents, except Cu, were strongly dependent on clay content (Table 1) resulting from the greater sorption capacity of soils richer in clay. Such soils have greater ability to accumulate air-borne metals as opposed to sandy soils that have metals moved deeper in the soil profile. Furthermore, finer-textured soils generally contain more metals of natural origin than sandy soils (Kabata-Pendias and Pendias, 2001). Copper was the only metal strongly correlated with soil organic carbon content, which reflects the affinity of this element for organic matter (Kabata-Pendias and Pendias, 2001). Copper was also weakly correlated with the contents of other metals (Table 1). Iron is not a metal posing any environmental risk. However, Fe was included because its determination might be useful for certain purposes; for example, Fe content in soil may affect bioavailability of other metals due to their occlusion by or adsorption on Fe oxides (Bruemmer et al., 1988).

Spectra

Near-infrared spectra were visually featureless showing only three very low bands over the spectral range most likely reflecting moisture-related absorption features (Fig. 4). However, derivative spectra (not shown) calculated from such data contain substantially more features on which calibrations can be based. Mid-infrared spectra, on the other hand, had significantly greater absorption values and had a greater number of features from 2400 to 500 cm^{-1}. Absorption bands in MIR are generally caused by fundamental molecular vibrations. Spectra of samples had generally similar shape within either spectral range (NIR or MIDIR), but had significantly different peak intensities. It may be found that the same type of chemical information is present in both the MIR and NIR spectral regions with the MIR spectra comprised largely of sharp bands from fundamental modes of vibration and NIR comprised of the muted overtones.

A standard use of mid-infrared spectral data has involved interpretation of spectral features for assessment of chemical structure and qualitative measure of sample composition. In the case of metal composition, the literature documents several spectral signatures associated with a large array of organometallic complexes (for review, see Nakamoto, 1997), which may occur in association with soil organic matter. Additionally, there is considerable information available on spectral signatures of various metal-containing minerals commonly found in soils and the technique has been used extensively in mineralogical studies of soil (Farmer, 1974). The emerging use of mid-infrared spectral data has been for quantification of sample properties by application of chemometrics. The use of chemometrics for quantification does not depend on a full understanding of the physical relationship between spectral data and chemical functional groups. Rather, it is based on mathematical relationships between spectra and reference data. The reliability
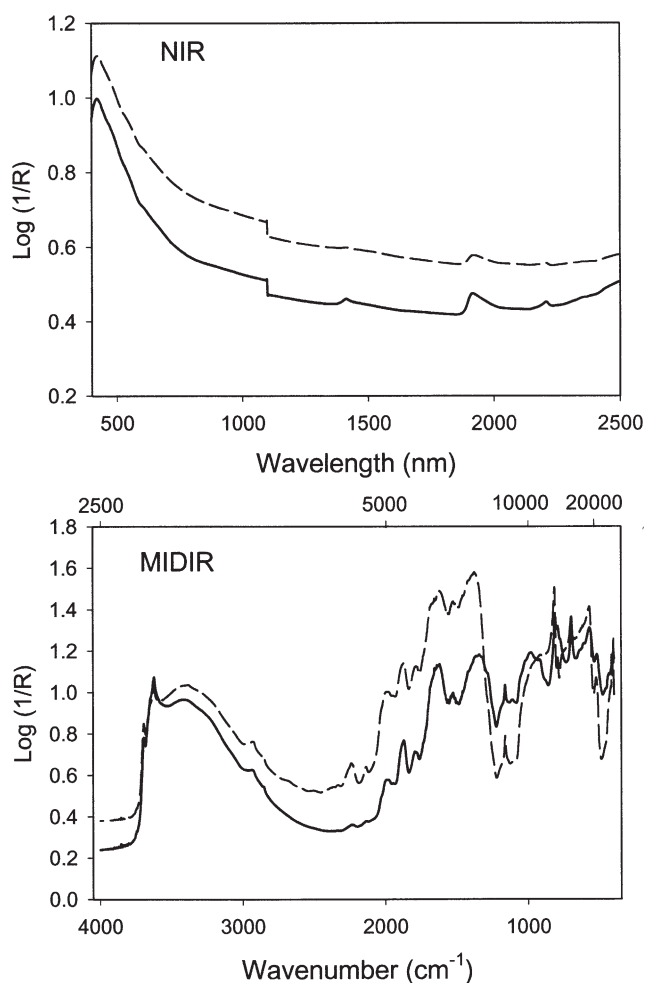

Fig. 4. Near-infrared (NIR) and mid-infrared (MIDIR) spectra of two samples selected at random from the data set.

of such predicted data can be assessed by use of cross-validation protocols. Although the gap in spectral understanding may be disconcerting for some researchers, the use of chemometrics for real-world applications has proven to be immensely successful (Williams and Norris, 2001). There is considerable risk in speculating on which spectral features that a multifactor PLS model uses for accurate predictions.

Near-Infrared Reflectance Spectroscopy Calibrations

Calibrations produced for total Cd, Cu, Pb, and Zn using NIRS were not satisfactory because there was a low R^2 between actual (chemically determined) and predicted contents. Predictions for Cu had a tendency to underpredict higher contents (more than 15 mg kg^{-1}) and overpredict lower contents (less than 10 mg kg^{-1}) (Fig. 5). The tendency for under prediction was also observed for Zn and Cd at the higher contents probably due to industrial contamination (Fig. 5). This fact may reduce the usefulness of NIR as a tool for indicating the most contaminated soils. Most samples with Pb contents below 1000 mg kg^{-1} were overpredicted, which was indicated by a low slope and large positive intercept (Table 2). The Pb predictions for more contaminated samples were inaccurate (Fig. 5). Calibrations were bet-
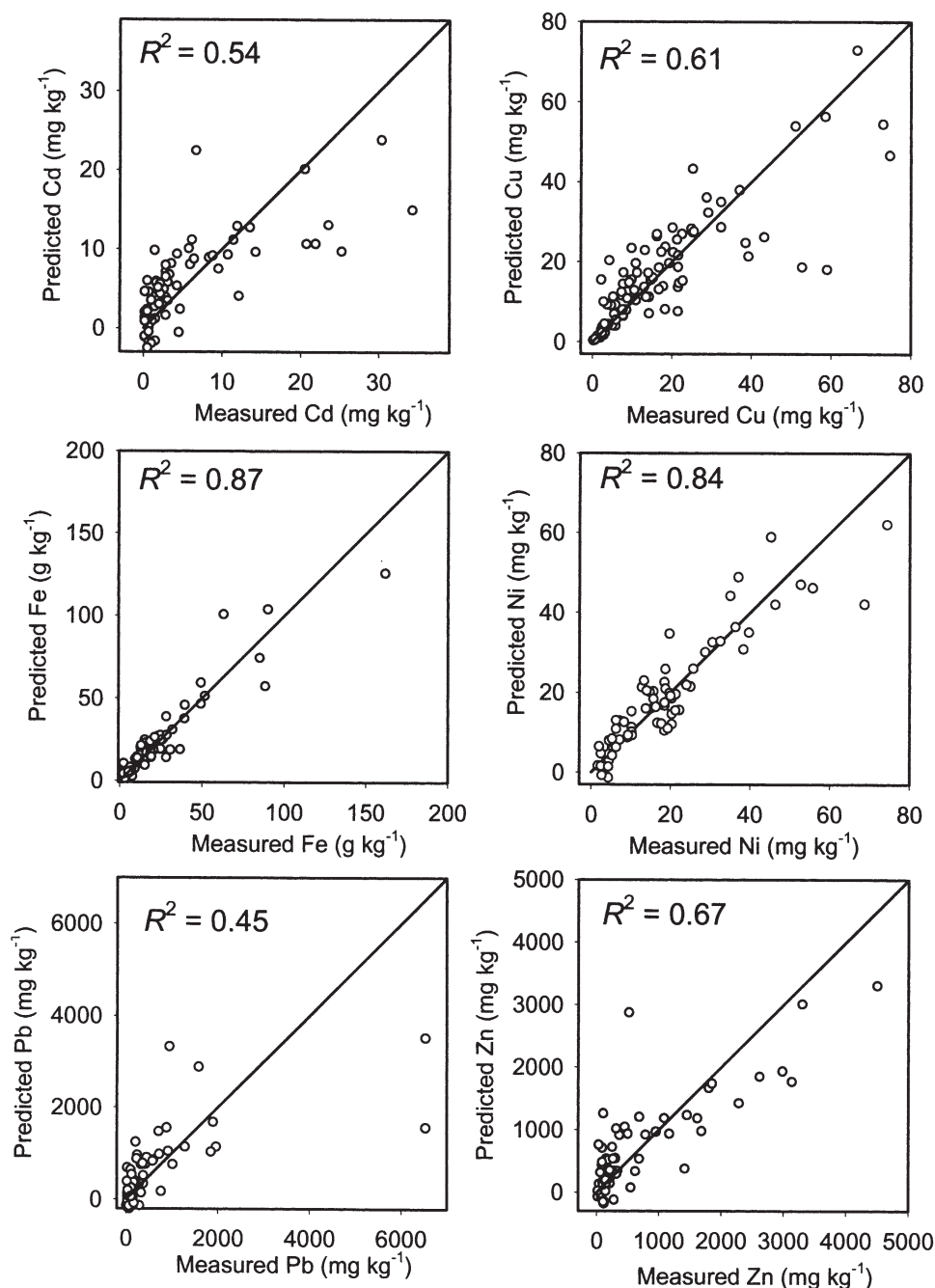

Fig. 5. The relationships between values measured by the standard procedure and predicted using near-infrared reflectance spectroscopy (NIRS).

Table 2. Calibration results based on near-infrared (NIR) spectra.

Metal	F†	PRE‡	R^2	Slope	Intercept	RMSD§	NRMSD¶
Fe	7	MV	0.87	0.87	3.01	9.2	0.40
Cd	3	MSC	0.54	0.54	2.56	5.13	0.92
Cu	6	M	0.61	0.61	8.15	10.3	0.49
Pb	3	MSC	0.45	0.45	286.9	839	1.61
Ni	7	M	0.84	0.84	3.12	6.21	0.29
Zn	4	MSC	0.67	0.67	207.0	526	0.84

† Number of factors.
‡ Spectral transformation. MV, mean and variance scaled; MSC, multiplicative scatter corrected; M, mean centered only.
§ Root mean squared deviation.
¶ Normalized parameter (NRMSD = RMSD/mean).

Table 4. Calibration results based on mid-infrared (MIDIR) spectra.

Metal	F†	PRE‡	R^2	Slope	Intercept	RMSD§	NRMSD¶
Fe	6	MSC	0.97	0.97	0.60	4.1	0.18
Cd	7	MV	0.94	0.94	0.32	1.82	0.33
Cu	9	MSC	0.80	0.80	4.32	7.52	0.36
Pb	5	MSC	0.66	0.66	178.7	662	1.27
Ni	14	–	0.99	0.98	0.29	1.88	0.09
Zn	13	MV	0.96	0.96	27.3	191	0.30

† Number of factors.
‡ Spectral transformation. MV, mean and variance scaled; MSC, multiplicative scatter corrected; M, mean centered only.
§ Root mean squared deviation.
¶ Normalized parameter (NRMSD = RMSD/mean).

ter for Fe and Ni. However, their R^2 values were still below 0.9 (Table 2). A normalized parameter, NRMSD (root mean squared deviation divided by mean of metal content; NRMSD = RMSD/mean) was used to compare accuracy of predictions for different metals that have different magnitudes of content. The NRMSD values were the lowest for Ni and Fe: 0.29 and 0.40, respectively, indicating the best accuracy of predictions (Table 2).

Samples poorly determined during the one-out cross-validation process are often called calibration outliers. These outliers can be defined when (i) the sample is spectrally different than the rest of the samples and (ii) the predicted content value is determined to have a residual difference significantly greater than those of other samples. In either case, the basis for the calibration outliers can be due to true sample differences, for example, a single sample with an analyte level much greater or lower than the rest of the dataset or due to errors or a poorly determined analyte value by standard chemical analysis. Removal of calibration outliers in most cases leads to improvement of predictions for samples remaining in the data set since calibrations are not burdened with less useful information. The algorithms within the Grams software (Galactic Industries, 1992) were used to identify and remove calibration outliers based on content and new calibrations were then developed. The removal of outlier samples from the data set improved accuracy of predictions for Cd, Cu, Fe, Pb, and Zn (RMSD significantly decreased for those metals; Tables 2 and 3). Only prediction models for Fe had R^2 values above 0.9 and R^2 for the Ni model increased from 0.77 to 0.84 although its RMSD did not greatly improve (Tables 2 and 3).

Diffuse Mid-Infrared Reflectance Spectroscopy Calibrations

Calibrations produced with MIDIR data performed substantially better than those with NIR for all metals

Table 3. Calibration results based on near-infrared (NIR) spectra after removal of calibration outliers.

Metal	F†	Samples removed	R^2	RMSD‡	Range§
Fe	9	13, 14, 15, 35, 44	0.94	3.7	2.2–90.0
Cd	5	1, 10, 14, 24, 35	0.80	2.54	0.17–30.3
Cu	7	14, 15, 32, 38, 57	0.75	6.01	2.2–66.5
Pb	5	13, 14, 15, 16, 20, 35	0.76	159	8.3–1583
Ni	4	13, 14, 44, 50, 57	0.77	6.01	1.7–55.7
Zn	6	13, 24, 35	0.84	299	14.7–3300

† Number of factors.
‡ Root mean squared deviation.
§ Metal content range after removal of outliers.

(Fig. 6). The RMSD values were substantially lower for DRIFTS calibrations (Tables 2 and 4). The most significant differences in accuracy of predictions between MIDIR and NIR were for Cd, Zn, and Ni in which RMSD decreased 2.75, 2.81, and 3.30 times, respectively. Comparison of the distribution of PLS residual errors for MIDIR and NIR calibrations shows substantially narrower spread of residuals for MIDIR for all predicted metals (Fig. 7). The much lower intercept values (Tables 2 and 4) indicate more accurate predictions using MIDIR for samples with lower metal contents. The most accurate MIDIR calibrations were produced for Cd, Fe, Ni, and Zn with NRMSD values from 0.09 to 0.33 (Table 4, Fig. 6). The R^2 value for Cu was lower than for the latter metals. However, the NRMSD value was only slightly worse (0.36), which indicates an accurate prediction for this metal (Table 4). Only Pb contents were still not predicted satisfactorily using MIDIR including most of the highly contaminated samples (Fig. 6). No relationship between chemically measured metal contents and residuals was observed for DRIFTS (Fig. 8). Removal of calibration outliers improved predictions for Pb with RMSD decreasing from 662 to 142 mg kg^{-1}. Predictions for Cd, Ni, and Zn were not improved most likely due to loss of some useful information linked to the removed samples (Tables 4 and 5).

The advantage of DRIFTS is probably related to more information existing in the mid-infrared region. Absorption bands in the MIDIR originate from fundamental vibrations while absorption spectra in NIR are basically overtones and combination bands (Ibanez and Cifuentes, 2001). In the analysis of organic substances such as forage, near-infrared spectra are known to be overtones and combination bands due to O–H, N–H, and C–H bonds of soil organic matter with no absorption bands due to mineral components (Shenk et al., 1992). Mid-infrared spectra contain the fundamental organic-related bands but also vibrations related to inorganic components, including anions such as phosphate and carbonate that absorb within the MIDIR region. Thus, there are more bands directly affected by metals in MIDIR and bands directly due to their salts, which may not be present in the NIR.

The strong absorption in the MIDIR range from spectra of undiluted samples has previously been recognized as a factor limiting application of DRIFTS to predict sample parameters. Dilution of samples with KBr consumes time and significantly increases the cost of analy-
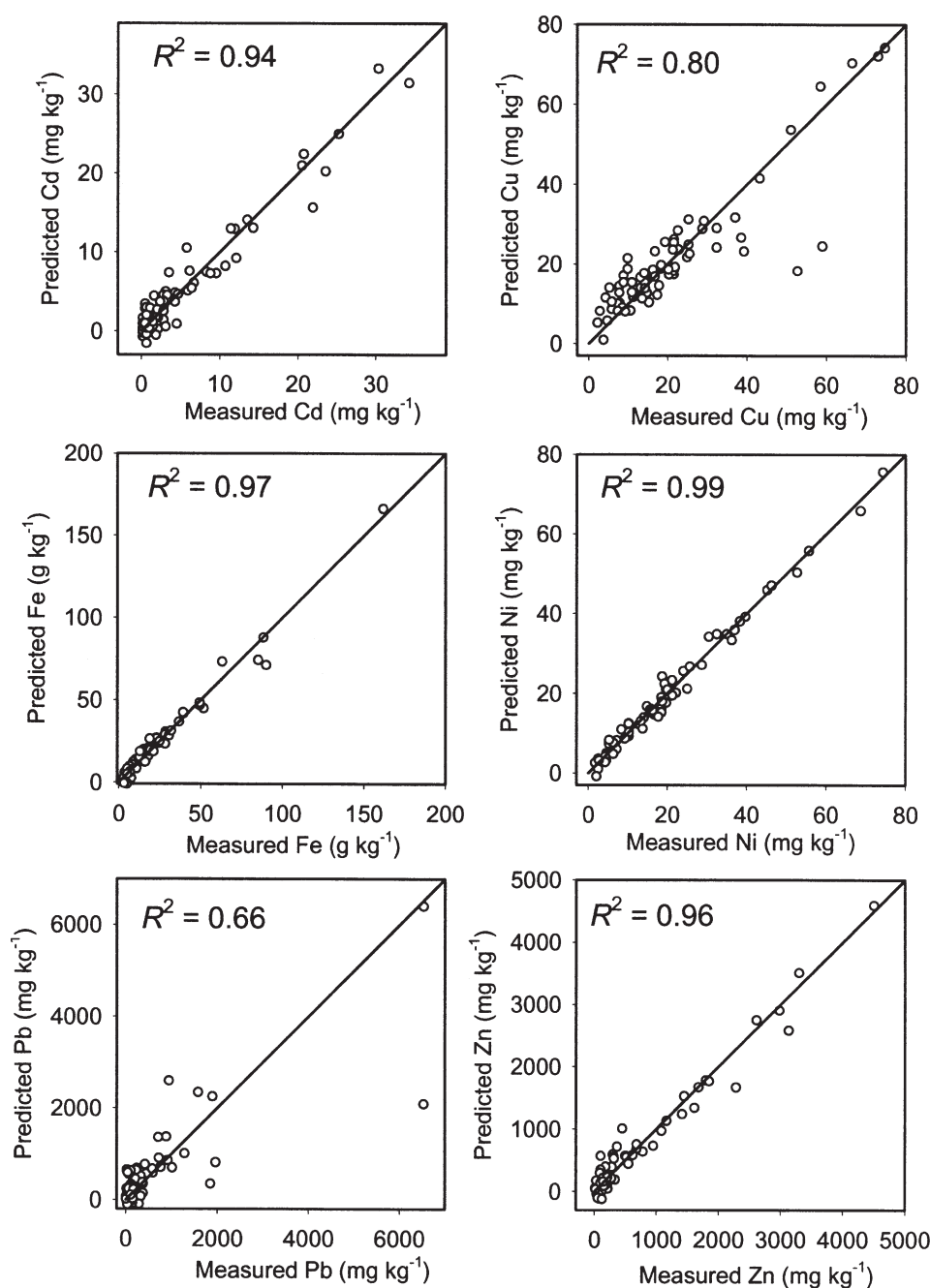
Fig. 6. The relationships between values measured by the standard procedure and predicted using diffuse mid-infrared reflectance spectroscopy (DRIFTS).

sis and would obviate the advantages of spectroscopic techniques such as quickness and low cost. However, several studies have demonstrated that accurate calibrations with MIDIR spectra can be developed without sample dilution (Nguyen et al., 1991; Reeves et al., 2001; McCarty et al., 2002; Reeves, 2003).

The correlation coefficients between absorbance and metal content over the spectral range are shown in Fig. 9 (NIR) and Fig. 10 (MIDIR). Correlation coefficients (r) for NIR reached high values (above 0.6) at three ranges of wavelengths: 490 to 580 nm (positive correlation), 795 to 830 nm (negative), and 1040 to 1210 nm for Cd, Zn, and Fe. Coefficients for other metals were

low over the entire range of spectra (Fig. 9). This fact does not strictly correspond to final calibration results because the best calibrations were produced for Fe and Ni. High correlation coefficients for MIDIR spectra were observed in many wavelengths over the entire spectral range and were the highest for Fe and Ni, which also produced the best MIDIR calibrations (Fig. 10). Interestingly, Pb was not predicted as well as Zn and Cd despite having very similar correlation results to those metals (Fig. 9 and 10), which could indicate that the same information was used for calibration equations produced for those three metals.

The coefficients of determination between actual and

predicted metal content and RMSD values in our study based on one-out cross validation provide strong evidence that samples not used in the calibration set might be predicted accurately (Table 6). One-out cross-validation predictions for each sample are based on equations produced using all other samples from the data set.

Characteristics of Calibration Outliers

In most cases, the same samples were classified as calibration outliers in NIR calibrations for particular metals, for example, Sample 14 (five metals), Samples 13 and 35 (four metals), and Sample 15 (three metals). The locations of samples that were calibration outliers

for at least two metals are indicated in Fig. 1. Most of those samples were located near Tarnowskie Gory and had extreme properties: high organic matter (Samples 14, 15, 57), high Fe (Samples 13, 14, 15), or high clay content (Sample 13). Removal of outliers of NIR calibrations significantly narrowed the predicted range of metal contents, especially for Pb and Zn, since the most contaminated soils were within removed samples (Table 3, Fig. 3). Mid-infrared-based calibrations exhibited better ability to predict metal contents in extreme samples. Only Sample 35 was the outlier for five metals. Other samples listed above appeared randomly. Sample 35 was collected in Miasteczko Slaskie. This sample
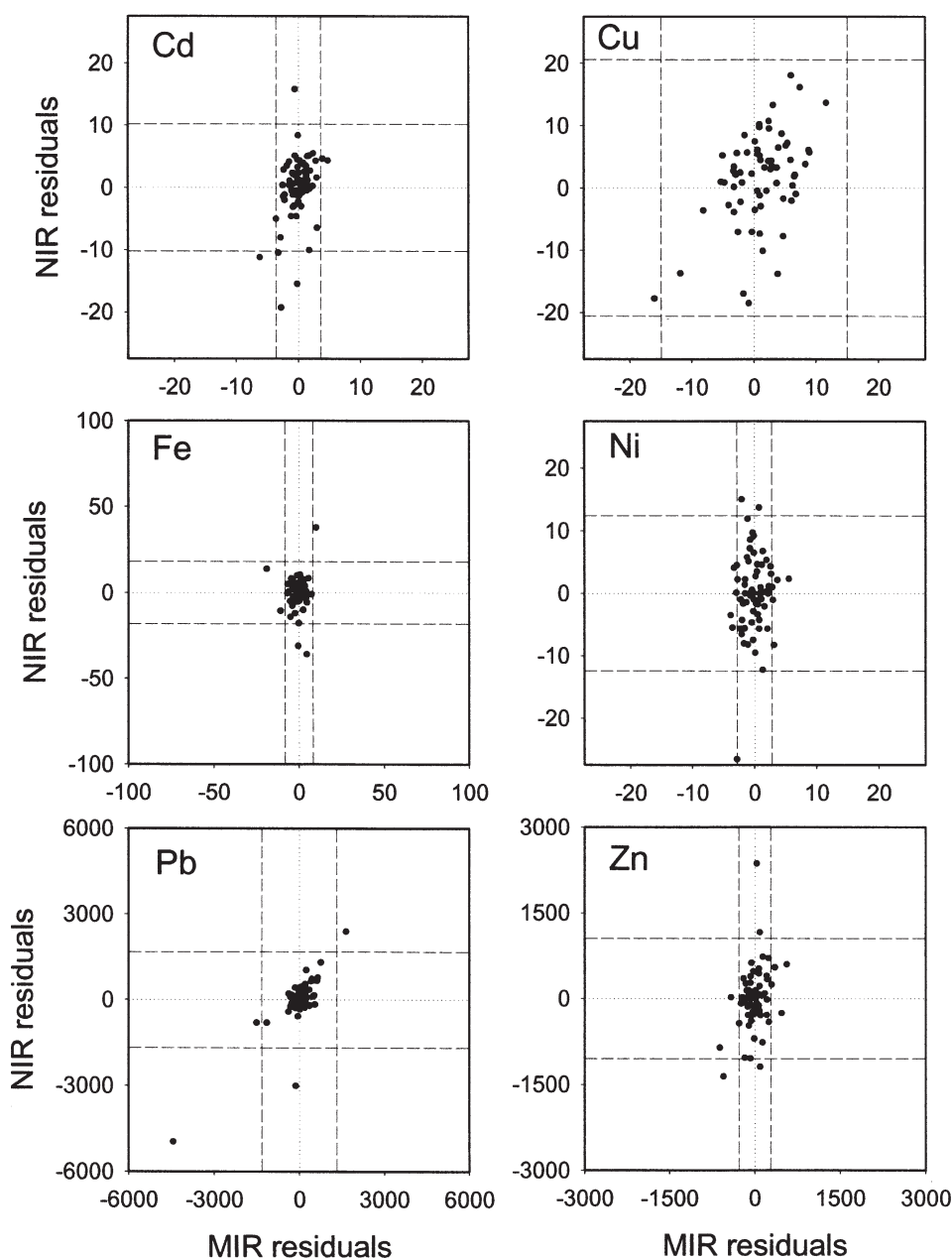

Fig. 7. Residual error distribution for diffuse mid-infrared reflectance spectroscopy (DRIFTS) and near-infrared spectroscopy (NIRS). Units for Cd, Cu, Ni, Pb, Zn are mg kg^{-1}; for Fe, g kg^{-1}. Dashed lines indicate standard deviations.

might have been spectrally different due to high Fe content or greater contribution of dust-borne metals in the total pool of metal in a soil as an effect of close distance to the zinc smelter. However, other samples collected in Miasteczko Slaskie were not defined as outliers. The MIDIR calibrations were also much better for prediction of the most contaminated soils. They were not removed as outliers, except two samples with the highest Pb content. The maximum predicted content for other metals after removal of outliers was equal to the

maximum content of the entire sample set (Table 5, Fig. 3).

The outlier samples described were outside the domain of properties typical to the overall population of collected samples. Most of the outliers were clustered to the south of Tarnowskie Gory. It is possible that larger representation of such samples would let one produce calibrations predicting even those samples accurately. The 70 soils used in the study certainly did not fully cover the diversity of soil properties for arable
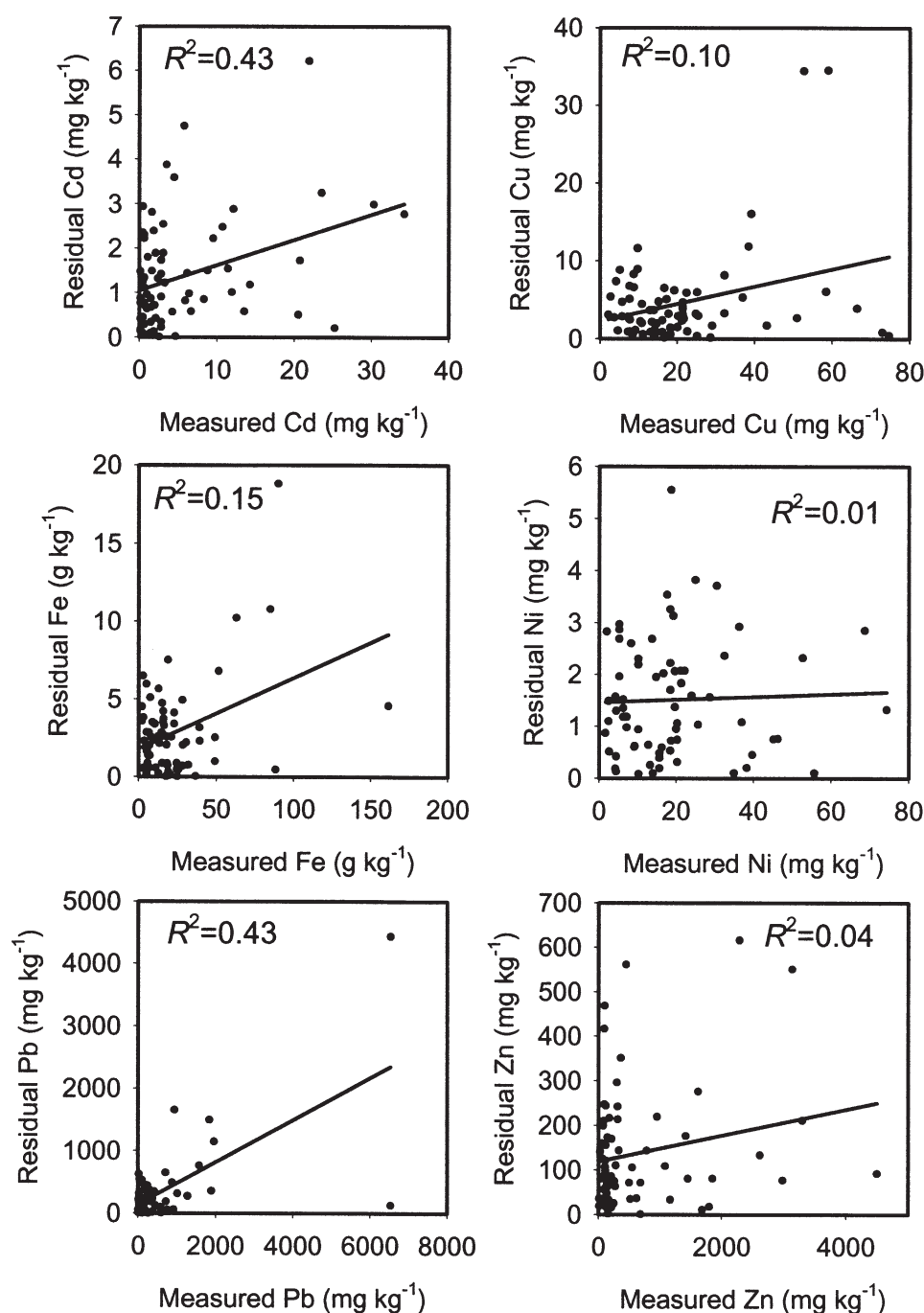

Fig. 8. The relationships between metal content measured by the standard procedure and residuals using diffuse mid-infrared reflectance spectroscopy (DRIFTS).

Table 5. Calibration results based on mid-infrared (MIDIR) spectra after removal of calibration outliers.

Metal	F†	Samples removed	R^2	RMSD‡	Range§
Fe	6	15, 23, 35, 69	0.98	2.9	2.2–161.7
Cd	4	1, 10, 14, 24, 35	0.90	1.83	0.17–30.3
Cu	10	32, 38, 55	0.95	3.58	2.2–74.7
Pb	7	13, 15, 16, 20, 35	0.86	142	8.3–1897
Ni	5	14, 35, 44, 50, 64	0.94	3.48	1.7–74.3
Zn	3	16, 24, 35	0.93	225	14.7–4500

† Number of factors.
‡ Root mean squared deviation.
§ Metal content range after removal of outliers.

lands of the Tarnowskie Gory region. However, it is also possible that two separate equations might be needed.

## Effect of Soil Properties on Accuracy of Predictions

As an example, the relationships between soil properties such as clay, carbon content, pH, and the accuracy of metal predictions are presented on Fig. 11 for Zn. All samples including outliers are included. Accuracy of prediction is expressed as percentage deviation from actual content. Negative values indicate underprediction of actual content, and positive values indicate over-

prediction. In the NIR and especially in the MIDIR region there is a clear relationship between soil texture and accuracy of predictions observed for all metals except Fe, which was predicted well over the entire range of clay content. In soils below 70 to 80 g of clay kg^{-1}, predictions of Cd, Zn, Cu, Ni, and Pb were more inaccurate. Light, sandy soils are usually low in metals so the less accurate predictions in such samples do not reduce the utility of the DRIFTS method for contaminated soils.

The reason for weaker predictions for coarser-textured soils is not clear. It might be due to weaker clay-related vibrations in such soils or different quality of organic matter in sandy soils. Furthermore, metals such as Zn and Cd are in these soils mainly present as forms immobilized by Fe oxides (Chlopecka et al., 1996) that might be well detected in the MIDIR (Kemper and Sommer, 2002). The higher the clay content in the soils studied the greater the percentage of Cd present in the fraction absorbed by Fe-oxides (Siebielec, 2001). This
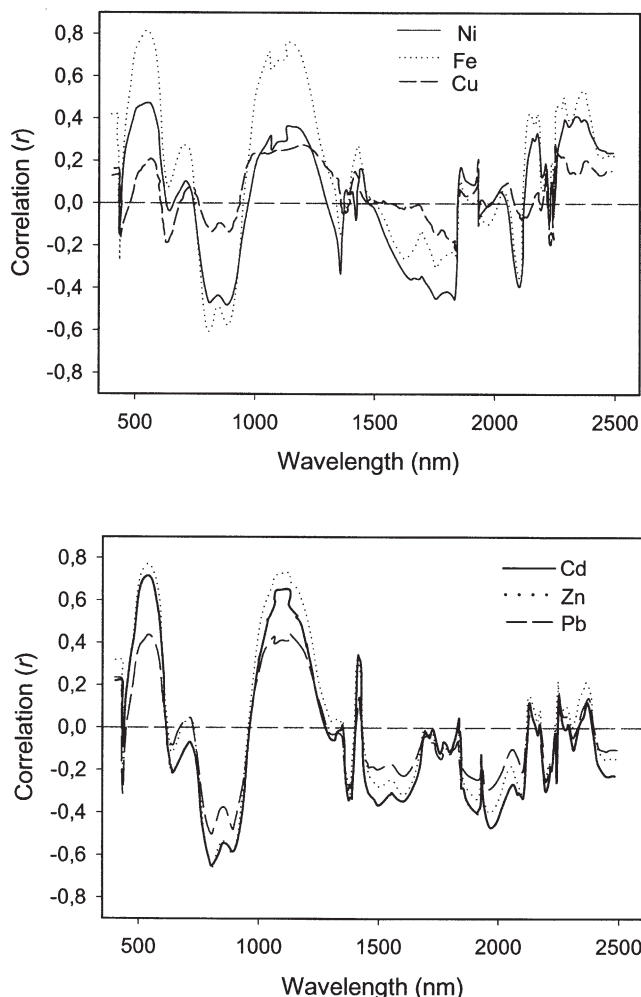
Fig. 9. Correlation coefficients between near-infrared (NIR) absorbance and metals content.
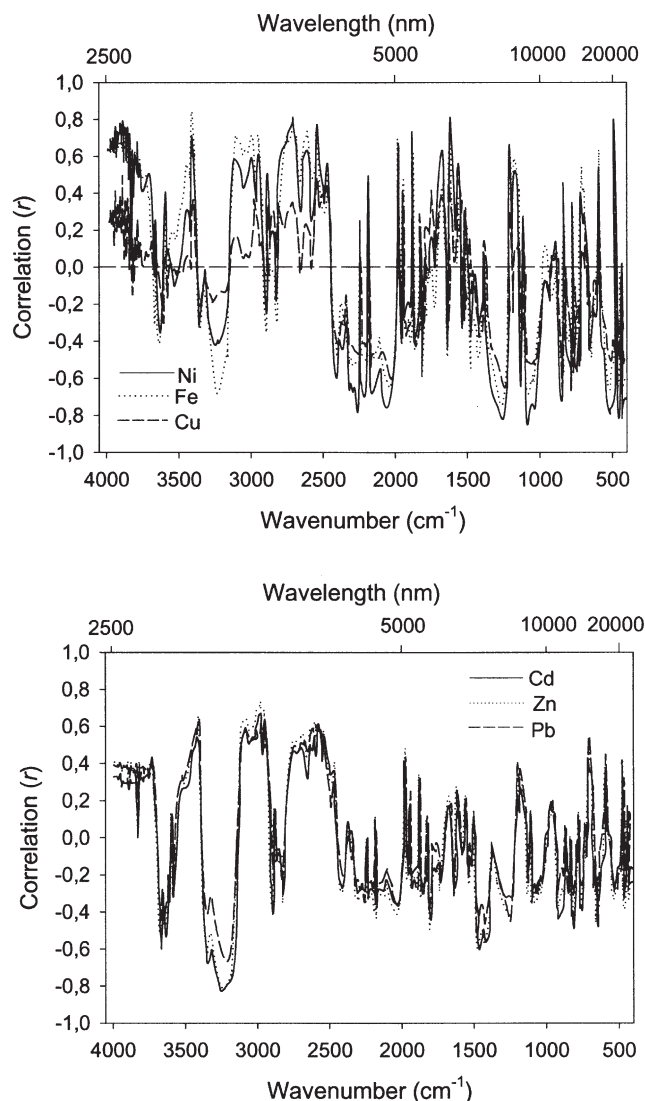
Fig. 10. Correlation coefficients between mid-infrared (MIDIR) absorbance and metals content.

supports the hypothesis that more accurate metal predictions in finer-textured soils could have been due to a stronger relationship between metals and Fe-oxides.

Carbon content at the range observed for most soils in our study (5.1–41.0 g kg^{-1}) seemed not to affect the accuracy of metal predictions in the MIDIR and NIR region (Fig. 11). Zinc and other metals in samples with the highest carbon content (53.3–73.2 g kg^{-1}) were predicted well in the MIDIR range if expressed as percent accuracy. No relationships between soil pH and accuracy of predictions were observed for all measured metals (Fig. 11).

CONCLUSIONS

Mid-infrared spectroscopy exhibited potential utility in detection of metal-contaminated soils. Results indicate that MIDIR may be used for quantitative measurements of metals in diverse soils if the calibration is developed from soils within the region. Proper and full representation of soil types and properties of the studied

Table 6. One-out cross validation results based on mid-infrared (MIDIR) spectra for all samples ($n = 70$) and after removal of calibration outliers.

Metal	All samples		After removal of outliers†	
	R^2	RMSD‡	R^2	RMSD
Fe	0.95	5.7	0.97	3.9
Cd	0.66	4.51	0.80	2.55
Cu	0.63	10.1	0.79	7.15
Pb	0.49	812	0.73	196
Ni	0.88	5.61	0.88	4.97
Zn	0.78	469	0.90	268

† Outlier samples listed in Table 5.
‡ Root mean squared deviation.

area seem to be important factors affecting calibration success. Larger sets of samples could improve overall predictions but in certain cases two separate calibrations might be needed to predict all samples accurately. Future work with larger sets of samples is needed. Poorer predictions for particular samples may result from a spectral difference in those samples or from inaccurate chemical analyses.
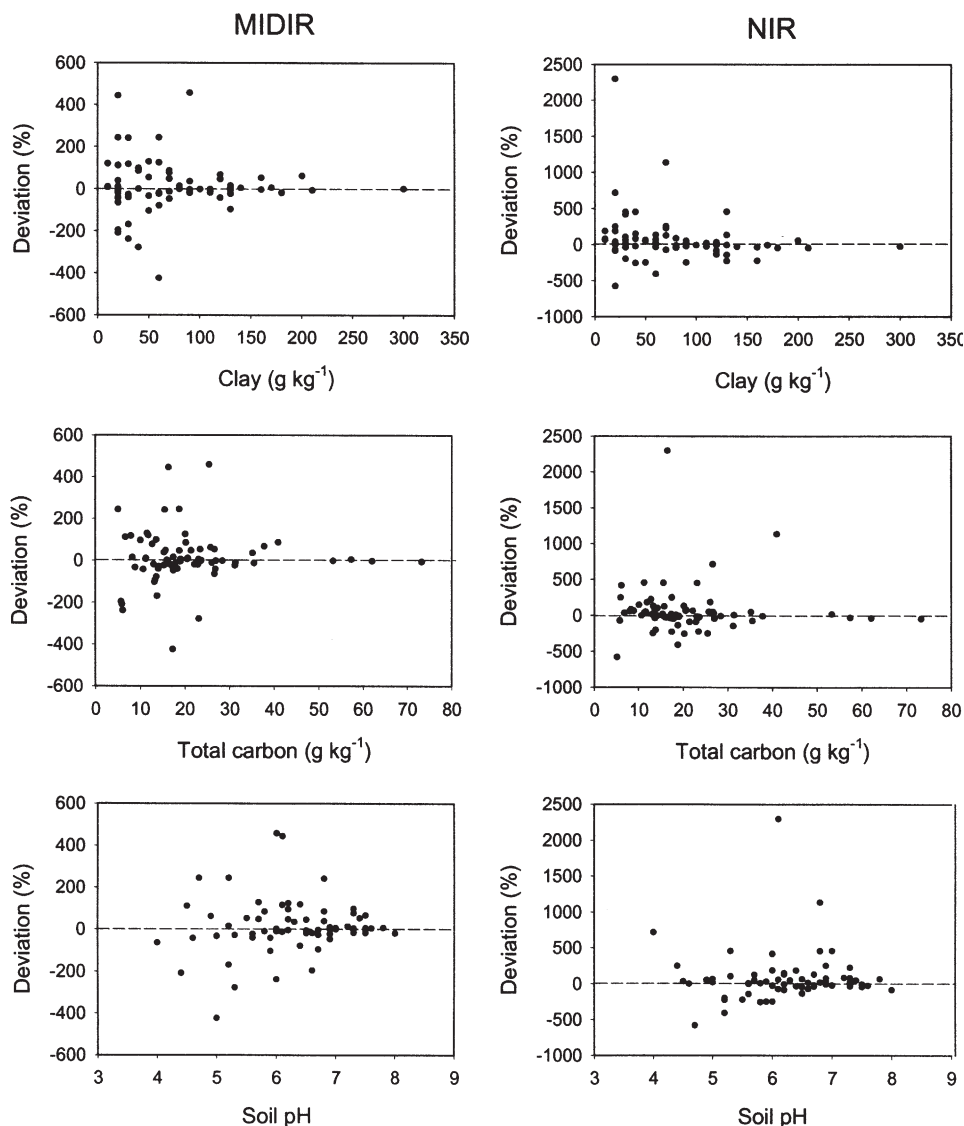
Fig. 11. The relationships between soil properties and accuracy of metal predictions using mid-infrared (MIDIR) and near-infrared (NIR) data.

It is difficult to fully assess the potential accuracy of MIDIR spectroscopy. It is possible that the accuracy of the spectral calibration may be limited by analytical error of the chemical assays used to develop the calibration. However, a much larger number of samples analyzable in MIDIR would provide more information at the region or landscape level than traditional chemical methods even if the technique was less accurate for particular samples. In environmental assessments, the uncertainty associated with spatial variance is often much greater than the uncertainty associated with analytical measurement. Calibrations based on chemical data obtained for 200 to 300 samples may be used for predictions of metal contents in perhaps thousands of other samples if the sample set used for calibrations was representative for overall population. The rapid and low cost spectral analyses can enable more effective environmental assessments. The method may be also useful for (i) indicating sites that should be analyzed by classical methods at the locations of samples with predicted high metal content and (ii) indicating samples that should be re-run by standard chemical methods as potentially inaccurately analyzed (i.e., samples that are inaccurately predicted in a calibration set).

Mid-infrared based calibrations substantially outperformed the more frequently used NIR. Mid-infrared based predictions were accurate both for metals with high range of content from low to high contamination (Cd, Zn, Pb) and for metals at background level of contamination (Cu, Ni). Our results also confirm that it is possible to obtain reliable calibrations using DRIFTS for diverse soils without sample dilution.

Soil pollution with metals in the Tarnowskie Gory region has a long-term character. Metals in these soils originate both from pedogenic sources and long-term exposure to industrial emissions. Metals from high-metal dust inputs have been subject to sorption, occlusion, and precipitation processes over decades. The calibrations developed in this study are probably only valid for soil polluted within the environment of occurrence and should not be extrapolated to soils that are newly contaminated. Results in such soils would be uncertain since the method is based on complex relationships between metals and various soil properties.

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